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RADIOMETRIC MEASUREMENT OF THORIUM AND EQUIVALENT URANIUM IN OKA-2 FOR CERTIFICATION PURPOSES

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ABSTRACT

The thorium and uranium contents of britholite ore reference material Oka-2 were measured by high-resolution gamma-ray spectrometry as a contribution to the interlaboratory certification project for this material conducted by the Canadian Certified Reference Materials Project. The results were 2.96 ± 0.02% thorium and 201 ± 3 µg/g uranium, where the precisions are standard deviations of the mean of five replicate sample determinations. Radium/uranium secular equilibrium is assumed in deriving the uranium content. The thorium/uranium ratio of 147 would appear to meet IAEA requirements to produce a gamma-ray calibration reference material from Oka-2.

DOSAGE RADIOMÉTRIQUE DU THORIUM ET DE L'URANIUM ÉQUIVALENT CONTENUS DANS L'OKA-2 POUR BUT D'HOMOLOGATION

par

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RÉSUMÉ

Dans le cadre du projet de certification inter-laboratoires pour le Programme canadien des matériaux de référence, on a mesuré les teneurs en thorium et en uranium contenus dans le minerai de britholite de référence Oka-2 par spectrométrie gamma à haute résolution. Les résultats ont été de 2.96 ± 0.02% pour le thorium et de 102 ± 3 µg/g pour l'uranium; les précisions sont l'écart-type de la moyenne de 5 déterminations pour chaque échantillon. Pour obtenir la teneur en uranium, on s'est basé sur l'hypothèse d'un équilibre séculaire radium/uranium. Le rapport thorium/uranium de 147 semble satisfaire aux exigences de l'AIEA pour la préparation d'un matériau de référence à partir du Oka-2 pour l'étalonnage des spectromètres gamma.

INTRODUCTION

Oka-2 is to be certified in 1985 for U, Th, K and lanthanides in an interlaboratory project. It is a thorium rare earth phosphate ore known as britholite. Because of its high thorium/uranium ratio, Oka-2 has been selected by IAEA as a source material to produce a reference material specifically for calibration of laboratory gamma-ray spectrometers. The IAEA standard is to be prepared by homogeneous dilution of Oka-2 with non-radiogenic silica.

As a contribution to this CCRMP certification project, thorium and equivalent uranium contents of Oka-2 were measured radiometrically employing high-resolution gamma-ray spectrometry. Results of these measurements are reported herein.

INSTRUMENTATION

All gamma-ray spectra were acquired using a Aptec germanium hyperpure detector of 20 cm^2 x 2.8 cm true coaxial configuration having a 0.5 mm thick aluminum end-window. Data analysis was accomplished with a Canberra Amplifier model 2020, a Canberra ADC/SCA model 8621 and a Canberra Series 85 multichannel analyser using 8192 channels over a 0-2626 KeV range. Parameters and characteristics of the photopeaks measured are presented in Table 1.

SAMPLE PREPARATION

Five 56 g aliquots of Oka-2 were compressed uniformly to fill identical 25 mL steel cans which were properly capped with steel lids and sealed tightly with epoxy glue.

STANDARD PREPARATION

Two thorium nitrate salts ($Th(NO_3)_4 \cdot 5H_2O$) from Amersham International Ltd. and Mackay Co. respectively were used to prepare calibration standards for thorium determination. Their thorium concentrations (established by gravimetry after ignition at 1000°C) were 40.60 (±0.07) % Th for Amersham

and 40.59 (±0.07) % Th for Mackay. The Amersham salt was refined in 1906 and is considered to be in secular equilibrium for thorium-232 and its daughters, but no date was specified for the Mackay salt and its secular equilibrium had to be evaluated. From economic considerations it was desirable to employ the less expensive Mackay salt for the spiking experiments. By comparison of intensities of two photopeaks (Ac-228 and Th-228) between solutions of the Amersham and Mackay salts, the Mackay thorium was determined to be only 96.5% in equilibrium and a correction was made in subsequent calculations.

CALIBRATION STANDARD PREPARATION

Two separate sets of calibration standards were required: one each for thorium and uranium determinations. For each set, calibration standards were prepared in two matrices: Oka-2 itself and SiO_2. Three different amounts of thorium standard were added to each matrix in the thorium determination according to the following procedure. A weighted amount of thorium standard (Amersham or Mackay) was dissolved in a small volume of water (2-4 mL) and the solution was transferred quantitatively on to the solid matrix in teflon beakers. Matrix and spike were then dried in a microwave oven and the dried material obtained was hand-ground and then blended using a mixer mill. A weighted fraction containing the equivalent of 56 g of Oka-2 or 45 g of SiO_2 was canned for gamma measurements (see Sample Preparation). Therefore, the cans contained equal amounts of matrix and various known amounts of added thorium and gamma-active daughters (see Tables 3 and 4).

For the uranium determination, one radium-226 addition was made to each matrix. They were prepared by drying 5 mL of 2000 pCi/mL radium-226 standard solution prepared from NBS SRM-4959 on the matrix and by following the same procedure as for thorium calibration standard (see Table 5).

ANALYTICAL MEASUREMENTS

Following an equilibration period exceeding 21 days, to permit radium-226/radon-222 daughter secular equilibrium to be attained, each can was mounted directly on the detector end window and the gamma spectrum was acquired typically for 7200 s (2 h).

The selection of gamma-ray lines was based on two major criteria: intensity and energy. The presence of heavy absorber lanthanides in Oka-2 had to be taken into account. Therefore, for the thorium determination, assuming a negligible matrix absorption effect at high energy, high energy analytical lines were preferred.

To provide improved precision for the equivalent thorium determination, three emission lines from thorium-daughters were used. For the uranium determination, four low and medium energy lines were selected because high energy emissions gave very low intensities (see Table 2 and Figure 1).

Two calibration methods were used for thorium determinations. The standard addition method was employed considering that, in theory, the gamma signals from spiked and unspiked samples should be subject to the same absorption and, therefore, be matrix-independent. However, considering that significantly different weight fractions of thorium were added to each spiked sample and thorium is a heavy absorber, the validity of this assumption had to be confirmed. For this reason, an independent calibration method with a silica matrix was applied. The same reasons justified two different calibration procedures for the uranium determination.

CALCULATIONS

The equivalent thorium concentration is calculated as:

$$C_{Th} = \frac{W_{Th} \times 100}{56}$$

where C_{Th} is the equivalent thorium concentration (% eTh), W_{Th}, the equivalent thorium weight in the can (g) and 56 is the total sample weight in the can (g).

The W_{Th} value from the standard addition method (Oka-2 matrix) is derived from a linear regression analysis where the net photopeak counting rate of each of the three spiked samples is entered as the dependent variable Y, and the weight of equivalent thorium added as the independent variable X. For each calculation, a zero addition point, represented by he net photopeak count rate of the unspiked sample (R_o) is included. The intercept on the X-axis gives the W_{Th} value. For the independent

calibration method (SiO_2 matrix), the net photopeak count rate per gram of equivalent thorium added is obtained for each of the three additions and the arithmetic mean is calculated. The W_{Th} value is given by the division of R_o by the mean value.

The equivalent uranium concentration is calculated as:

$$C_U = \frac{W_U \times 100}{56}$$

where C_U is the equivalent uranium concentration (% eU), W_U, the equivalent uranium weight in can (g) and 56, the total sample weight in can (g).

W_U is derived from:

$$W_U = \frac{W_{Ra} \times A_{Ra}}{A_U}$$

where W_{Ra} is the weight of radium-226 found in the can (pg), A_{Ra} is the specific activity of radium-226 (3.659×10^{-2} Bq/ng) and A_U, the specific activity of uranium-238 (1.2346×10^{4} Bq/g of total uranium). The ratio A_{Ra}/A_U is thus the number of grams of uranium per nanogram of radium, assuming secular equilibrium exists between uranium-238 and radium-226. W_{Ra} is the result of dividing R_o* bythe net count rate per picogram of radium-226 added (N). R_o* is the net photopeak count rate of the unspiked sample less the thorium contribution (see Table 6). N is obtained from:

SiO_2 calibration $$N = \frac{R_A}{W_A}$$

Oka-2 calibration $$N = \frac{R_A - R_o^*}{W_A}$$

where R_A is the net photopeak count rate of the spiked sample less the thorium contribution and, W_A, the weight of radium-226 added.

DISCUSSION OF RESULTS AND CONCLUSIONS

The values of thorium concentration obtained for Oka-2 are reported in Table 7. The concentrations calculated from the two calibration methods are in reasonable agreement, but differ by more than the estimated statistical errors. These results confirm that, even at high energies, the matrix absorption effects are not negligible. However, it can be noted that the matrix effects diminish as energy increases. It is also possible to observe that SiO_2 is less absorbing than Oka-2 and, therefore, produces a higher intensity for the same amount of eTh. For this reason, the results of the standard addition method should be more accurate. In fact, a correction for absorption difference would have to be applied to obtain accurate results from the SiO_2 calibration.

The values of uranium concentration and eTh/eU ratio obtained for Oka-2 are reported in Table 8. The 1120 KeV line data were ignored in the calculations because of low intensities and high estimated statistical errors. The uranium concentration results calculated by the two calibration methods are in good agreement within the estimated statistical errors. The ratio results confirm the high eTh/eU of Oka-2 and for the reason mentioned before for the thorium concentration, the ratio calculated from the standard addition method should be more accurate.

Table 1 - Characteristics and measurement parameters of photopeaks employed for the measurement of isotope concentrations

	Thorium Daughters			Uranium Daughters			
Isotope	^{228}Ac	^{228}Ac	^{208}Tl	^{214}Pb	^{214}Pb	^{214}Bi	^{214}Bi
Energy (KeV)	911.2	968.9	2614.5	295.4	352.0	609.3	1120.0
Centroid (KeV)[1]	911.7	969.8	2616.5	295.4	352.1	609.7	1121.0
ROI (KeV)	907.4-916.4	961.2-973.7	2610.1-2623.2[2]	292.2-298.0	347.3-355.3	606.2-612.9	1116.6-1126.3
Interval (KeV)	9.0	12.5	13.1	5.8	8.0	6.7	9.7

(1) Due to temperature instability in the laboratory, small centroid shifts (±0.3KeV) between measurements were noted and therefore, these values are averages.

(2) In an attempt to correct for energy calibration variations, the ROI interval of 13.1 KeV was adjusted symmetrically about the centroid.

Table 2 - Gamma-ray measurement data of unspiked samples

Sample	Mass g	Net Photopeak Count Rate counts per second (±2σ%)						
		Thorium daughters			Uranium daughters			
	Isot. KeV	^{228}Ac 911.2	^{228}Ac 968.9	^{208}Tl 2614.5	^{214}Pb 295.4	^{214}Pb 352.0	^{214}Bi 609.3	^{214}Bi 1120.0
Oka-2 A	56	16.47(0.6)	12.48(0.8)	6.72(0.9)	0.874(11.9)	1.445(8.5)	0.985(7.9)	0.236(18.3)
Oka-2 B	56	16.26(0.6)	12.35(0.8)	6.71(0.9)	0.933(11.1)	1.456(8.3)	0.962(8.0)	0.231(18.7)
Oka-2 C	56	16.36(0.6)	12.43(0.8)	6.74(0.9)	0.951(11.0)	1.442(8.5)	0.942(8.3)	0.202(21.9)
Oka-2 D	56	16.42(0.6)	12.41(0.8)	6.78(0.9)	0.865(12.1)	1.490(8.2)	0.941(8.3)	0.222(20.1)
Oka-2 E	56	16.70(0.6)	12.51(0.8)	6.83(0.9)	0.932(11.2)	1.482(8.3)	0.974(8.0)	0.270(15.8)
	mean (S.D)	16.44(0.16)	12.44(0.06)	6.76(0.05)	0.911(0.039)	1.463(0.022)	0.961(0.019)	0.232(0.025)

Table 3 - Gamma-ray measurement data of thorium spiked samples, Oka-2 matrix

Standard	Addition g eTh	Oka-2 Matrix g		Photopeak Count Rate counts per second (±2σ%)		
			Isot. KeV	^{228}Ac 911.2	^{228}Ac 968.9	^{208}Tl 2614.5
Mackay	0.3593	56		20.12(0.5)	15.27(0.7)	8.28(0.8)
Mackay	0.3593	56		19.99(0.5)	15.23(0.7)	8.24(0.8)
Mackay	0.3593	56		20.12(0.5)	15.22(0.7)	8.30(0.8)
			mean (±2σ)	20.08(0.06)	15.24(0.06)	8.27(0.04)
Mackay	0.7186	56		23.86(0.5)	17.95(0.6)	9.84(0.8)
Mackay	0.7186	56		23.63(0.5)	17.93(0.6)	9.68(0.8)
			mean (±2σ)	23.74(0.08)	17.94(0.08)	9.76(0.06)
Mackay	1.437	56		30.81(0.4)	23.33(0.6)	12.75(0.7)
Mackay	1.437	56		30.55(0.4)	23.13(0.6)	12.62(0.7)
			mean (±2σ)	30.68(0.09)	23.23(0.10)	12.68(0.08)

Table 4 - Gamma-ray measurement data of thorium spiked samples, SiO_2 matrix

Standard	Addition g eTh	SiO_2 Matrix g		Photopeak Count Rate counts per second (±2σ%)		
			Isot. KeV	^{228}Ac 911.2	^{228}Ac 968.9	^{208}Tl 2614.5
Amersham	0.40654	45		4.22(1.2)	3.15(1.6)	1.69(1.9)
Amersham	0.40654	45		4.21(1.2)	3.19(1.6)	1.70(1.9)
			mean (±2σ)	4.22(0.04)	3.17(0.04)	1.70(0.02)
Amersham	0.8129	45		8.20(0.9)	6.25(1.1)	3.41(1.3)
Amersham	0.8129	45		8.21(0.9)	6.20(1.1)	3.42(1.3)
			mean (±2σ)	8.20(0.05)	6.22(0.05)	3.42(0.03)
Mackay	1.4607	45		15.02(0.6)	11.38(0.8)	-
Mackay	1.4607	45		15.14(0.6)	11.40(0.8)	6.09(1.0)
Mackay	1.4607	45		15.06(0.6)	11.54(0.8)	6.11(1.0)
			mean (±2σ)	15.07(0.05)	11.44(0.05)	6.10(0.04)

Table 5 - Gamma-ray measurement data of radium spiked samples

Matrix	Mass g	NBS Ra-226 Addition picograms	Photopeak Count Rate counts per second (±2σ%)			
		Isot. KeV	^{214}Pb 295.4	^{214}Pb 352.0	^{214}Bi 609.3	^{214}Bi 1120.0
Oka-2	56	9716	3.03(3.7)	5.02(2.6)	3.20(2.7)	0.62(7.9)
			3.04(3.7)	5.07(2.6)	3.20(2.7)	0.67(7.3)
			3.03(3.8)	5.08(2.7)	3.24(2.7)	0.65(7.6)
			2.99(3.8)	5.12(2.6)	3.27(2.7)	0.66(7.4)
		mean (±2σ)	3.02(0.05)	5.07(0.07)	3.23(0.04)	0.65(0.02)
SiO_2	45	9880	2.25(1.8)	3.58(1.4)	2.18(1.7)	0.38(5.1)
			2.28(1.8)	3.60(1.4)	2.13(1.7)	0.38(5.1)
			2.23(1.8)	3.49(1.4)	2.12(1.7)	0.38(4.8)
			2.24(1.8)	3.56(1.4)	2.14(1.7)	0.38(5.1)
		mean (±2σ)	2.25(0.02)	3.55(0.02)	2.14(0.02)	0.38(0.01)

Table 6 - Gamma-ray measurement data of thorium spiked samples, SiO_2 matrix (used for thorium contribution correction in eU calculations)

Standard	Addition g eTh	SiO_2 Matrix g		Photopeak Count Rate counts per second (±2σ%)			
			Isot. KeV	^{214}Pb 295.4	^{214}Pb 352.0	^{214}Bi 609.3	^{214}Bi 1120.0
Amersham	0.40654	45		0.092(56.0)	0.113(52.9)	0.061(61.9)	0.035(58.5)
Amersham	0.40654	45		0.068(75.7)	0.113(52.6)	0.075(49.9)	0.030(70.7)
			mean	0.080	0.113	0.068	0.032
Amersham	0.8129	45		0.119(60.3)	0.170(49.1)	0.158(33.1)	0.073(38.9)
Amersham	0.8129	45		0.069(>100)	0.141(59.8)	0.137(38.5)	0.076(37.4)
			mean	0.094	0.155	0.148	0.074
MacKay	1.4607	45		0.037(>100)	0.084(>100)	0.091(78.1)	0.093(43.7)
MacKay	1.4607	45		0.024(>100)	0.014(>100)	0.081(88.7)	0.087(45.8)
MacKay	1.4607	45		0.017(>100)	0.082(>100)	0.105(68.2)	0.099(40.9)
			mean	0.026	0.060	0.092	0.093
			mean of 7	0.061	0.102	0.101	0.070

Table 7 - Results of gamma-ray measurements of thorium concentration in Oka-2

Calibration	Sample	Thorium Concentration in Sample % eTh (±2σ)			
		Isot. KeV	^{228}Ac 911.2	^{228}Ac 968.9	^{208}Tl 2614.5	Mean of 3 (S.D.)
Oka-2 spiked[1]	Oka-2 A		2.98(0.07)	2.99(0.06)	2.92(0.04)	2.96(0.04)
	Oka-2 B		2.93(0.07)	2.95(0.06)	2.90(0.04)	2.93(0.03)
	Oka-2 C		2.95(0.07)	2.98(0.06)	2.93(0.04)	2.95(0.03)
	Oka-2 D		2.97(0.07)	2.97(0.06)	2.95(0.04)	2.96(0.01)
	Oka-2 E		3.05(0.07)	3.01(0.06)	2.99(0.04)	3.02(0.03)
	mean of 5 (S.D.)(±2σ of mean)					2.96(0.03)(0.02)
SiO_2 spiked[2]	Oka-2 A		2.87(0.03)	2.87(0.03)	2.87(0.03)	2.87(0.00)
	Oka-2 B		2.83(0.03)	2.84(0.03)	2.86(0.03)	2.84(0.02)
	Oka-2 C		2.85(0.03)	2.86(0.03)	2.88(0.03)	2.86(0.02)
	Oka-2 D		2.86(0.03)	2.86(0.03)	2.89(0.03)	2.87(0.02)
	Oka-2 E		2.91(0.03)	2.88(0.03)	2.92(0.03)	2.90(0.02)
	mean of 5 (S.D.)(±2σ of mean)					2.87(0.02)(0.01)

(1) Calculations were based on standard addition method using linear regression of 3 standard additions plus a zero addition (Oka-2 alone) for each aliquot of Oka-2 (CPS versus g eTh added).

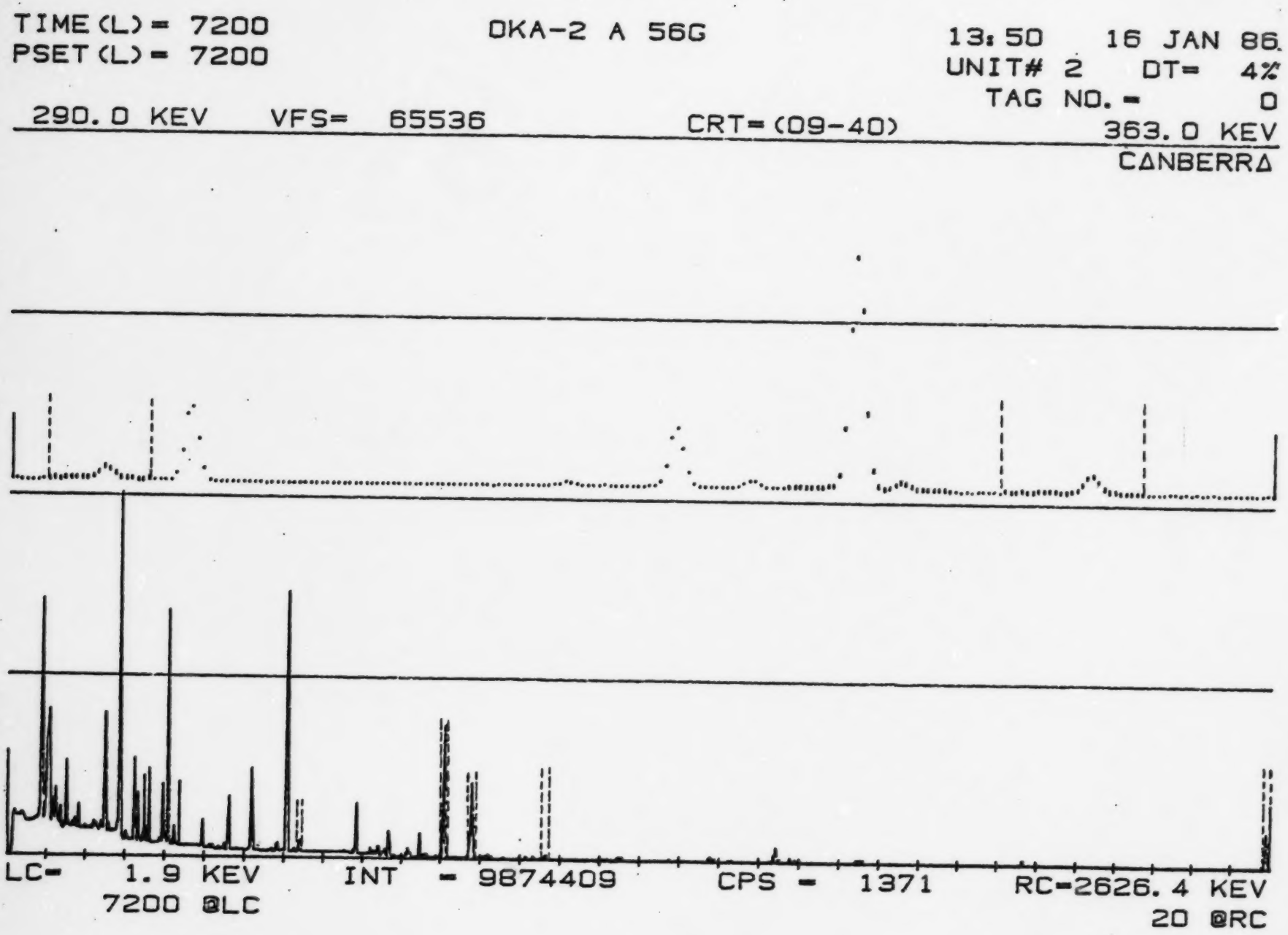
(2) Calculations were done by using, for each photopeak, the mean of CPS/g eTh values of 3 spiked additions to SiO_2 matrix.

Table 8 - Results of gamma-ray measurements of uranium concentration in Oka-2

Calibration	Sample	Uranium Concentration in Sample % eU (±2σ)					eTh/eU (±2σ)
		Isot. KeV	^{214}Pb 295.4	^{214}Pb 352.0	^{214}Bi 609.3	^{214}Bi 1120.0	Mean of 3 [1] (S.D.)
Oka-2 spiked	Oka-2 A		0.0198(.0026)	0.0191(.0018)	0.0200(.0018)	0.0204(.0055)	0.0196(.0012)
	Oka-2 B		0.0212(.0026)	0.0193(.0018)	0.0195(.0018)	0.0197(.0055)	0.0200(.0012)
	Oka-2 C		0.0217(.0026)	0.0191(.0018)	0.0191(.0018)	0.0162(.0055)	0.0200(.0012)
	Oka-2 D		0.0196(.0026)	0.0198(.0018)	0.0190(.0018)	0.0186(.0055)	0.0195(.0012)
	Oka-2 E		0.0212(.0026)	0.0197(.0018)	0.0198(.0018)	0.0245(.0055)	0.0202(.0012)
	mean of 5 (S.D.)						0.0199(0.0003)
	(±2σ of mean)						(0.0005)
							149(4)
SiO_2 spiked	Oka-2 A		0.0189(.0024)	0.0198(.0018)	0.0216(.0019)	0.0230(.0053)	0.0201(.0012)
	Oka-2 B		0.0203(.0024)	0.0199(.0018)	0.0210(.0019)	0.0222(.0053)	0.0204(.0012)
	Oka-2 C		0.0207(.0024)	0.0197(.0018)	0.0205(.0019)	0.0182(.0053)	0.0203(.0012)
	Oka-2 D		0.0187(.0024)	0.0204(.0018)	0.0205(.0019)	0.0209(.0053)	0.0199(.0012)
	Oka-2 E		0.0203(.0024)	0.0203(.0018)	0.0213(.0019)	0.0275(.0053)	0.0206(.0012)
	mean of 5 (S.D.)						0.0203(0.0003)
	(±2σ of mean)						(0.0005)
							141(4)

(1) Mean of 3 peak values: 295.4 KeV, 352.0 KeV and 609.3 KeV.

FIGURE 1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